REMARKS

Reconsideration and allowance of this application is respectfully requested in light of the following remarks.

Status of Claims

Claims 1-3 and 6-11 stand rejected under 35 U.S.C. 102(b) as being anticipated by JP-10-017694, claims 4 and 5 stand rejected under 35 U.S.C. 102(b) as being anticipated by JP-10-017694 or in the alternative as being obvious from JP-10-017694.

Section 102 Rejection

Claims 1-11 of the Instant Invention stand rejected under 35 U.S.C. 102(b), as being anticipated by JP-10-017694. Applicant traverses this rejection.

With respect to claims 1-8, the Examiner is reminded that, new uses for compositions of matter are clearly allowable under the 35 USC, as can be demonstrated by the definition of the term process under 35 USC § 100(b) which reads:

(b) The term "process" means process, art or method, and includes a new use of a known process, machine, manufacture, composition of matter, or material.

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The current claims pending under this Official Action are drawn as method claims to a new use of a known composition of matter or material. Therefore they are essentially a new use for a known material which are clearly allowable under 35 USC § 100(b).

According to *LANDIS ON THE MECHANICS OF PATENT CLAIM DRAFTING*, Fourth Edition, Copyright 1996, §56 ". . . a "new use" claim, which is nothing more than an ordinary method claim, the main difference being that the novel feature is not, or need not be, in the manipulative steps of the method. Rather, the novelty may reside in the use of the old composition for a new purpose." " The test of patentability becomes obviousness of the new use, since a novel process is defined." Landis §56. "If the composition were previously used as a cleaning solution, it presumably would be unobvious to employ it as an electroplating solution." Landis §56.

In the Instant Invention the microporous sheet comprising a blend of an aliphatic polyolefin and a thermoplastic olefin elastomer is a known composition of matter or material, however "the method of improving the mechanical strength of a membrane comprising the step of: providing" constitutes a new use. The Claim is written in proper method or process format in accordance with 35 USC § 100(b).

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Presently claims 1-8 stand rejected as anticipated, under Section 102(b) over JP 10-017694. To anticipate a claim, a single source must contain all of the elements of the claim. *See Hybritech Inc. v. Monoclonal Antibodies, Inc.,* 802 F.2d 1367, 1379, 231 USPQ 81, 90 (Fed. Cir. 1986); *Atlas Powder Co. v. E.I. du Pont De Nemours & Co.,* 750 F.2d 1569, 1574, 224 USPQ 409, 411 (Fed. Cir. 1984); *In re Marshall,* 578 F.2d 301, 304, 198 USPQ 344, 346 (C.C.P.A. 1978). Missing elements may not be supplied by the knowledge of one skilled in the art or the disclosure of another reference. *See Structural Rubber Prods. Co. v. Park Rubber Co.,* 749 F.2d 707, 716, 223 USPQ 1264, 1271 (Fed. Cir. 1984). Where a reference discloses less than all of the claimed elements, an Examiner may only rely on 35 USC § 103. *See Titanium Metals Corp. v. Banner,* 778 F.2d 775, 780, 227 USPQ 773, 777 (Fed. Cir. 1985).

The JP 10-017694 reference fails to teach a method of improving the mechanical strength of a membrane. The case law is clear that missing elements may not be supplied by the knowledge of one skilled in the art or the disclosure of another reference. *See Structural Rubber Prods. Co. v. Park Rubber Co.,* 749 F.2d 707, 716, 223 USPQ 1264, 1271 (Fed. Cir. 1984). In the Instant Application it is clear that improving the mechanical strength was demonstrated by an increase in tensile strength shown in Table 1.

Therefore claims 1-8 should be clearly patentable over JP-10-017694 under 35 USC §102(b).

With respect to claims 9-11, clam 9 was amended to more clearly set forth the features of the Instant Invention. Support for this amendment can be found on page 7 of the Instant Specification as filed. No new matter has been added. Specifically the Instant Invention is produced by a dry stretch process. This differs from the solvent extraction technique of the prior art reference JP 10-017694 as described on pages 7 and 8 of the translation.

In amended claim 9 the clause of the claim, "a dry stretched microporous sheet" is a structural term. In re Steppan 156 USPQ 143, 148 (CCPA 1967), and In re Garnero 162 USPQ 221, 223 (CCPA 1969). In Steppan, the court viewed the "product-by-process" language, i.e. "condensation product," as a further qualifier of the invention. In the instant claim, the questioned language further defines the microporous sheet as a particular type of microporous sheet, i.e. "dry-stretched" microporous sheet. The other way to get a microporous sheet would be to use the solvent extraction technique outline in JP 10-017694. Both methods are recognized, in the art, as descriptors of different classes or methods for producing a microporous sheet. See Synthetic Polymer Membranes A Structural Perspective, by Robert E. Kesting, Second Edition, Copyright 1985, where the dry stretched process is

described on pages 290-297 and where the solvent extraction by the wet process is described on pages 251-261. These pages not only discuss the differences in the two processes but also discuss the physical differences in the end products.

In Garnero, the court compared the "product-by-process" language, i.e. "interbonded," to a list of words that had previously been construed as structural terms. Appellant maintains that the amended clause, "dry stretched" is a modifier of a noun that structurally defines that noun, just as the words reviewed in Garnero. Thus, the questioned clauses are structural elements of the claim and cannot be disregarded when considering patentability of the claims.

As amended, claims 9-11 should be clearly patentable over JP-10-017694 under 35 USC §102(b).

Section 103 Rejection

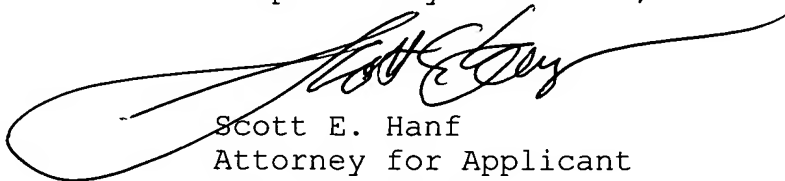Claims 4 and 5 are also alternatively rejected under 35 USC § 103(a) as being obvious from JP 10-017694, Applicants traverse. Claims 4 and 5 depend from claim 1 which should be allowable for the reasons set forth above. Therefore claims 4 and 5 should be equally allowable with claim 1. Dependent claims are nonobvious under section 103 if the independent claims from which they

depend are nonobvious. *Hartness Int'l, Inc. v. Simplimatic Eng'g Co., 819 F.2d 1100, 1108, 2 USPQ2d 1826, 1831 (Fed. Cir. 1987); In re Abele, 684 F.2d 902, 910, 214 USPQ 682, 689 (CCPA 1982); see also In re Sernaker, 702 F.2d 989, 991, 217 USPQ 1, 3 (Fed. Cir. 1983).*

Conclusion

In view of the foregoing, the applicant respectfully requests an early Notice of Allowance in the instant application.

Respectfully submitted,

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Attachments: Tranlation of JP10-017694A   (16 pages)
                    Synthetic Polymer Membranes   (12 pages)

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(19) Japanese Patent Office (JP) (12) Official Gazette for Laid-Open Patent Applications (A) (11) Japanese Unexamined Patent Application (Kokai) No. **10-17694**

(43) Disclosure Date: January 20, 1998

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(21) Application No.: 8-194058 (22) Filing Date: July 5, 1996	(71) Applicant: 000000033 Asahi Chemical Industry Co., Ltd. (72) Inventor: Takahiko Kondo (72) Inventor: Takuya Hasegawa (74) Agent: Takeshi Shimizu, Patent Attorney (and two others)

(54)   [Title of the Invention]   **Microporous Polyethylene Membrane**

(57)   [Abstract]

[Object]   To provide a microporous polyethylene membrane that has better workability and results in better productivity, and that has high heat resistance capable of ensuring greater battery safety under stringent conditions.

[Means]   A more heat-resistant microporous polyethylene membrane having a strain-hardening elongation viscosity, a gel fraction of less than 1%, and an average pore diameter of 0.001 to 0.1 µm; a battery separator using it; and a battery using the battery separator.

[Merit]   The better workability and productivity, and the higher heat resistance of the membrane allow more reliable batteries to be produced when it is used as battery separator.

[Claims]

[Claim 1]   A more heat-resistant microporous polyethylene membrane, characterized by having a strain-hardening elongation viscosity, a gel fraction of less than 1%, and an average pore diameter of 0.001 to 0.1 μm.

[Claim 2]   A battery separator featuring the use of a microporous polyethylene membrane according to Claim 1.

[Claim 3]   A battery featuring the use of a battery separator according to Claim 2.

[Detailed Description of the Invention]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a microporous polyethylene membrane suitable for use as a battery separator.

[0002]

[Prior Art]

Progress has recently been made in increasing the capacity of batteries, such as lithium ion batteries. As a result, an increasingly important issue has become battery safety during malfunctions such as short circuits. Microporous polyethylene membranes have been used as separators in such high capacity batteries, particularly lithium ion batteries. Such microporous polyethylene membranes are used because of their general properties, such as their mechanical strength and permeability, as well as their ability to develop the "Fuse Effect," where the separator melts to form a film covering the electrodes and cuts off the current when the battery internally overheats, thereby ensuring battery safety.

[0003]

Microporous polyethylene membranes are known to have a fuse temperature, which is the temperature at which the fuse effect takes place, of around 130 to 150°C. If for some reason the battery internally overheats, the current is shut down and the battery reaction is stopped when the fuse temperature is reached. However, the fuse effect can sometimes fail to take place in time when the temperature increases rapidly or the like. That is because the separator stretches and becomes broken due to the contracting force that is produced when the separator melts or due to the pressure persisting between the electrodes after the melt down, resulting in shorts between the positive and negative electrodes. Cross linked microporous polyethylene membranes have

been used recently to endow separators with better heat resistance capable of ensuring battery safety even under more stringent conditions such as the above.

[0004]

Problems, however, with all conventional methods for cross linking microporous polyolefin membranes are that the gel content complicates processes such as stretching, the production efficiency is compromised, and so forth. Japanese Unexamined Patent Application (Kokai) 1-167344, for example, discloses a method for cross linking microporous polyolefin membranes with cross linkers, but the microporous polyolefin membrane obtained by this method contains an abundance of gel, complicating the stretching process and the like, and does not give a membrane with high strength.

[0005]

Japanese Unexamined Patent Application (Kokai) 56-73856 discloses a method for cross linking microporous polyolefin membranes by means of ionizing radiation, but the microporous polyolefin membrane obtained by this method also contains gel. Other problems are the need for a high energy process, which causes the polyolefin to heat up while irradiated, so that the microporous membrane sometimes melts or shrinks. A necessary remedy is to separately carry out a number of treatments with lower energy.

[0006]

[Problems Which the Invention Is Intended to Solve]

An object of the invention is to provide a microporous polyethylene membrane that has better workability and results in better productivity, and that has high heat resistance capable of ensuring greater battery safety under stringent conditions.

[0007]

[Means for Solving the Abovementioned Problems]

As a result of extensive research undertaken to address the objects of the invention, the present invention was perfected upon the discovery that microporous polyethylene membranes characterized by specific thermal deformation behavior had higher heat resistance, with a gel fraction of less than 1%, resulting in better workability and productivity, as compared to microporous membranes lacking such behavior. That is, the first of the inventions is a microporous polyethylene membrane, characterized by strain-hardening during the measurement of elongation viscosity, and a gel fraction of less than 1%, preferably with an average pore

diameter of 0.001 to 0.1 μm, as determined by a permeability method. The second of the inventions is a battery separator featuring the use of such a microporous polyethylene membrane. The third of the inventions is a battery featuring the use of such a battery separator.

[0008]

The invention is described in detail below. The microporous polyethylene membrane of the invention is described first. Although it is not clearly understood why the microporous polyethylene membrane with strain-hardening properties and a gel fraction of less than 1% has high heat resistance, the heat resistance as determined in overcharging tests and breaking tests at elevated temperature, for example, can be dramatically improved in comparison to ordinary microporous polyethylene membranes lacking such strain-hardening properties. The method for endowing membranes with such strain-hardening properties is simple and does not compromise the workability or productivity of conventional membranes.

[0009]

The elongation viscosity is a physical constant with a considerable effect on melt tension during extension and deformation. It can be readily determined with a commercially available elongation viscosity meter (such as the Melten Rheometer by Toyo Seiki), and is normally expressed as a function of strain rate and time. As illustrated in Figure 2, the elongation viscosity of a molten microporous polyethylene membrane which normally contains no gel increases, when stretched at a constant strain rate from a relatively fixed point, until it is dependent on the strain rate, and then tends to decrease precipitously as it approaches breakage. This type of breakage is referred to as ductile fracture.

[0010]

As illustrated in Figure 1, on the other hand, the elongation viscosity of the molten microporous polyethylene membrane of the invention increases longer than the normal type when stretched under the same conditions, tending to increase at a linear or greater rate near the breaking point until sudden breakage. This type of breakage is referred to as elastic break. These properties indicate strain-hardening properties. Details on elongation viscosity can be found, for example, in Kiyohito Koyama, *Journal of the Japanese Society of Rheology*, **19**, 174 (1991). The gel fraction is determined based on ASTM D2765. The gel fraction in the invention is less than 1%. A gel fraction of 1% or more makes processes such as stretching more difficult and lowers productivity.

[0011]

The heat resistance of a separator made of the microporous membrane of the invention is comprehensively evaluated in accelerated tests involving heating tests as well as external short and overcharging tests on batteries assembled using the separator. As a result of detailed study o the breaking behavior of the membrane after melting, the inventors found that the results of the accelerated tests wee strongly correlated to the break time in silicon oil at 160°C.

[0012]

That is, the microporous polyethylene membrane of the invention has a break time of at least 20 seconds in 160°C silicon oil. Such membranes passed all of the above accelerated tests. Conventional microporous polyethylene membranes, on the other hand, all failed one or more of the accelerated tests, with a break time of 20 seconds or less, which was consistent with the results of the accelerated tests. That is, a characteristic feature of the microporous polyethylene membrane of the invention is the break time in 160°C silicon oil.

[0013]

The microporous polyethylene membrane of the invention thus has high heat resistance, but with an air permeability of no more than 2000 seconds, as determined on the basis of 25 μ, and a breaking strength of at least 500 kg/cm^2, resulting in far better heat resistance as well as mechanical strength and permeability than conventional microporous polyethylene membranes. The polyethylene used in the invention should be high density polyethylene, which is a crystalline polymer based on ethylene. Blends with no more than 30% polyolefin, such as polypropylene, medium density polyethylene, linear low density polyethylene, low density polyethylene, and EPR may also be used.

[0014]

The weight average molecular weight of the polyethylene should be 100,000 to 4,000,000, preferably 200,000 to 1,000,000, and even more preferably 200,000 to 700,000. A molecular weight under 100,000 tends to result in breakage during stretching, while more than 4,000,000 will complicate the manufacture of hot solution. The weight average molecular weight may be adjusted to within the desired range by blending polyethylenes of different molecular weight, by multiple stage polymerization, or the like. The membrane should be 1 to 200 μm thick, and preferably 10 to 50 μm thick. Less than 1 μm will result in unsatisfactory mechanical

strength, while more than 200 μm will cause problems when attempting to make lighter, more compact batteries.

[0015]

The air permeability should be 20 to 80%, and preferably 30 to 60%. Less than 20% will result in poor permeability, while more than 80% will not result in satisfactory mechanical strength. The mean pore diameter should be 0.001 to 0.1 μm, preferably 0.005 to 0.5 μm, and even more preferably 0.01 to 0.03 μm. A mean pore diameter under 0.001 μm will result in poor permeability, while more than 0.1 μm will slow down the interruption of the current through the fuse effect, with a risk of short circuits caused by deteriorating electrolyte or precipitated dendrites.

[0016]

A method for producing the microporous polyethylene membrane of the invention is described below. The method comprises the following three steps of forming the membrane, stretching it, and extracting it.

Forming the Membrane

A polymer gel, which is an intermediate in the invention, is produced by dissolving polyethylene in a plasticizer at or over the melting point to produce a hot solution which is then cooled to no more than the crystallization temperature. The plasticizer referred to here is an organic compound capable of forming a homogenous solution with polyethylene at a temperature no greater than the boiling point. Specific examples include decalin, xylene, dioctyl phthalate, dibutyl phthalate, stearyl alcohol, oleyl alcohol, decyl alcohol, nonyl alcohol, diphenyl ether, n-decane, n-dodecane, and paraffin oil, paraffin oil and dioctyl phthalate are preferred. The proportion of plasticizer is not particularly limited, but is preferably 20% to 90%, and more preferably 50% to 70%. Less than 20% will interfere with achieving a suitable porosity, while more than 90% will result in a lower viscosity which will complicate continuous formation.

[0017]

The polymer gel is formed into a sheet with a thickness in the tens of μm to tens of mm. This is the starting sheet, and the step for producing it is referred to as the membrane-forming step. The method for forming the membrane is not particularly limited. An example is to feed the plasticizer and high density polyethylene powder to an extruder where the ingredients are melt

kneaded at about 200°C, and to then cast the mixture from a common coat-hanger die onto a cooling roll, thereby continuously forming membranes.

[0018]   Stretching Step

The starting sheet is then stretched at least uniaxially to produce an oriented membrane. The stretching method is not particularly limited. Tenters, rolls, calendaring, and the like can be used. Biaxial stretching with tenters is preferred. The stretching temperature can range from ambient temperature to the melting point of the polymer gel, preferably from 80 to 130°C, and even more preferably from 100 to 125°C. The draw ratio should be 4 to 400-fold, preferably 8 to 200-fold, and even more preferably 16 to 100-fold, based on area. A draw ratio of less than 4-fold will not produce satisfactory separator strength, while more than 400-fold will make stretching difficult and will result in a lower porosity, etc.

[0019]   Extraction Step

The plasticizer is then extracted from the drawn membrane to produce a microporous membrane. The extraction method is not particularly limited. When paraffin oil or dioctyl phthalate are used, they can be extracted with an organic solvent such as methylene chloride or methyl ethyl ketone (MEK), and then removed when heated and dried at a temperature no greater then the fuse temperature. When a low boiling compound such as decalin is used as the plasticizer, it can be removed by being heated and dried at a temperature no greater then the fuse temperature. In either case, the membrane should be restrained to prevent adverse effects on physical properties caused by membrane shrinkage. To endow the membrane with strain-hardening properties, a treatment with an organic peroxide should be performed during the membrane-forming step, or treatment with ionizing radiation should be performed after any step.

[0020]   Treatment With Organic Peroxide

A certain amount of an organic peroxide is added to the polyethylene or plasticizer, the ingredients are melt kneaded to produce a hot solution at conditions under which the peroxide does not substantially decompose, the hot solution is heated to the temperature at which the organic peroxide decomposes, and it is cooled to at least the polyethylene crystallization temperature, resulting in a peroxide-treated starting sheet. A microporous polyethylene membrane with strain-hardening properties can be produced through the stretching and extraction steps.

[0021]

The expression "peroxide does not substantially decompose" means that the active oxygen of the peroxide does not fall below ½ during the time until a homogenous hot solution is prepared from the polyethylene, plasticizer, and organic peroxide. For example, if it takes 10 minutes to melt knead the ingredients, they should be melt kneaded at a temperature no greater than one resulting in a peroxide half life of 10 minutes, so that a homogenous hot solution can be prepared without the peroxide substantially decomposing. The half life is the time in which the amount of active oxygen reaches falls to ½ when a benzene solution of 0.1 mol/L organic peroxide is allowed to decompose at a given temperature.

[0022]

The organic peroxides referred to here are peroxy ketals, dialkyl peroxides, peroxy esters, and the like with a half life of 1 minute or more at 150°C. Examples include α,α'-bis (t-butylperoxy)diisopropyl benzene, dicumyl peroxide, 2,5-dimethyl-2,5-bis (t-butylperoxy)hexane, t-butyl cumyl peroxide, di-t-butyl peroxide, and 2,5-dimethyl-2,5-bis (t-butylperoxy)hexane-3. The proportion of the organic peroxide is not particularly limited, but is preferably 0.001% to 1%, and more preferably 0.01% to 0.5%. Less than 0.001% will result in unsatisfactory heat resistance, while more than 1% will result in insoluble gel components in the plasticizer, making it difficult to process the solution into a uniform membrane.

[0023]

Polyfunctional monomer may be added in a proportion no greater than 1%. Examples of polyfunctional monomers include divinyl benzene, diallyl phthalate, triallyl cyanurate, and triallyl isocyanurate. For example, a plasticizer in which the organic peroxide has been dissolved and high density polyethylene powder can be fed to an extruder, they can be melt kneaded at a temperature at or over the polyethylene melting point but no greater than one resulting in an organic peroxide half life of 10 minutes, and the hot solution can be cast onto a cooling roll from a common coat-hanger die heated to at least a temperature at which the organic peroxide half life will be 10 seconds, so as to continuously form membranes.

[0024]   Electron Beam Treatment

The material can be endowed with strain-hardening properties by ionizing radiation treatment after any of the steps in the method for producing conventional microporous polyethylene membranes noted above. Treatment after extraction by ion beam treatment is preferred. The radiation during ion beam treatment should be 0.1 to 10 Mrad, and preferably 1 to

5 Mrad. Too little radiation will not improve the heat resistance enough, while too much will cause the microporous polyethylene membrane to be heated by the ion beam energy, so that the membrane sometimes melts or shrinks. The strain-hardening properties can thus be readily provided without significantly affecting normal manufacture and productivity.

[0025]

[Embodiments of the Invention]

Embodiments of the invention are described in detail below. The following tests were conducted in the examples.

1) Membrane Thickness

Measured using a dial gage (Peacock No. 25 by Ozaki Seisakusho).

2) Porosity

This was determined by the following equation from the volume and weight of 20 cm square samples.

Porosity (%) = {volume (cm^3) – weight (g)/0.95)/volume (cm^3)} × 100

[0026]   3) Mean Pore Diameter

When an aqueous solution of 0.05 wt% pullulan (by Showa Denko) was circulated at a differential pressure of 0.5 kg/cm^2, the concentration of pullulan contained in the filtrate was determined from the differential refractive index. The mean pore diameter (μm) was calculated using the following equation from the molecular weight M of pullulan at 50% inhibition and the intrinsic viscosity {η} of the same aqueous solution.

$$[\eta] M = 2.1 \times 10^{4} ((d/2)^{1})^{1/1}$$

4) Gel Fraction

This was determined by the following equation as the ratio of the post-extraction residual mass relative to sample mass prior to extraction based on the change in weight upon the extraction of components solubilized after 12 hours in boiling para-xylene based on ASTM D2765.

Gel fraction (%) = residual mass (g)/sample mass (g) × 100

[0027]   5) Puncture Strength

A puncture test was conducted at a puncture speed of 2 mm/sec with a needle tip radius of 0.5 mm using a KES-G5 Handy Compression Tester by Kato Tech. The greatest puncture load

was considered the puncture strength (g). The puncture strength was multiplied by the membrane thickness (μm)/25 (μm) to calculate the puncture strength in terms of 25 μ.

6) Air Permeability

This was determined with a Gurley air permeability meter based on JIS P-8117. The air permeability was multiplied by membrane thickness (μm)/25 (μm) to calculate the air permeability in terms of 25 μ.

[0028]   7) Elongation Viscosity

The microporous membranes were dipped in 150°C silicon oil to relax the orientation, and the elongation viscosity was determined at a strain rate of 0.1/sec using a melt elongation flow measuring device (Melten Rheometer by Toyo Seiki). The presence or absence of strain-hardening properties was determined by the type of breakage. For example, stretching a conventional microporous polyethylene membrane results in neck-in about midway through in the sample, with a precipitous decrease in the elongation viscosity at a certain time before breakage (ductile fracture), whereas the elongation viscosity of microporous polyethylene membranes endowed with strain-hardening properties increases continuously until breakage (elastic break).

8) Membrane Break Test

A microporous polyethylene membrane was secured between two stainless steel washers with an outside diameter of 25 mm, this was held down at four peripheral points by clips, and it was dipped in 160°C silicon oil (KF-96-10CS, by Shin-Etsu Kagaku). Membranes which broke within 20 seconds, as determined by macroscopic assessment, were rated ×, those which did not break were rated O.

[0029]   9) Overcharging Test

Lithium ion batteries were produced using $LiCoO_2$ as the positive electrode active material, graphite and acetylene black as the conductor, and fluorine rubber as the adhesive, resulting in an 88:7.5:2.5:2 weight ratio mixture of $LiCoO_2$:graphite:acetylene black:fluorine rubber, which was applied in the form of a dimethyl formamide paste onto aluminum foil and dried. The resulting sheet was used as the positive electrode. A 95:5 weight ratio mixture of needle coke and fluorine rubber was applied in the form of a dimethyl formamide paste onto copper foil and dried. The resulting sheet was used as the negative electrode. Lithium borofluoride was adjusted to a concentration of 1.0 M in a propylene carbonate and butyrolactone

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solvent mixture (volumetric ratio = 1:1) as the electrolyte. The batteries were charged for 5 hours at 4.2 V, and were then overcharged at a constant current. The overcharging caused the interior of the batteries to heat up. The current was shut down when the fuse temperature was reached. Samples in which no current was restored 1 hour or later were rated O. Because these were accelerated tests, they were conducted without any of the safety features such as PTC elements which are normally set up in actual batteries.

[0030]   Example 1

40 parts high density polyethylene with a weight average molecular weight of 250,000, 60 parts paraffin oil (P350P by Matsumura Petroleum), and 0.2 part dicumyl peroxide (150°C half life about 10 min, 200°C half life about 7 sec) were kneaded for 5 min at 150°C and 50 rpm in a batch type melt kneader (Labo Plastomill by Toyo Seiki). The resulting kneaded mixture was molded with a 200°C heated press, heated as such for 10 minutes, and then cooled with a water-cooled press, giving a 1000 µm thick starting sheet. This was drawn at 120°C to a factor of 6 × 6 using a simultaneous biaxial stretching machine (by Toyo Seiki), and the paraffin oil was then extracted with methylene chloride. The properties of the resulting microporous polyethylene membrane are given in Table 1.

[0031]   Example 2

A microporous polyethylene membrane was produced in the same manner as in Example 1 except that 0.8 part dicumyl peroxide was used. The properties of the resulting microporous polyethylene membrane are given in Table 1.

Comparative Example 1

A microporous polyethylene membrane was produced in the same manner as in Example 1 except that no organic peroxide was added. The properties of the resulting microporous polyethylene membrane are given in Table 1.

Comparative Example 2

An attempt was made to produce a microporous polyethylene membrane in the same manner as in Example 1 except that 6 parts organic peroxide was added, but considerable stretching stress caused the membrane to break, and the membrane could not be processed to the required draw ratio.

[0032]

[Table 1]

	Example 1	Example 2	Comp. Ex. 1	Comp. Ex. 2
membrane thickness (μm)	25	28	24	--
porosity (%)	40	38	45	--
pore diameter (μm)	0.03	0.02	0.04	--
puncture strength (g/25 μ)	400	450	300	--
air permeability (sec/25 μ)	620	710	470	--
gel fraction (%)	0	0	0	20
strain-hardening	yes	yes	no	--
break test (160°C)	O	O	×	--

[0033]   Example 3

40 parts high density polyethylene with a weight average molecular weight of 250,000, 60 parts paraffin oil (P350P by Matsumura Petroleum), and 0.4 part dicumyl peroxide were kneaded at 150°C a in a 35 mm biaxial extruder, and the kneaded mixture was cast from a 200°C coat-hanger die (1400 μm lip interval) onto a cooling roll adjusted to 30°C to produce a 1400 μm thick starting sheet. The sheet was stretched at 120°C to a factor of 7 × 7 using a simultaneous biaxial stretching machine, and the paraffin oil was then extracted with methylene chloride. The properties of the resulting microporous polyethylene membrane are given in Table 2.

[0034]   Example 4

40 parts high density polyethylene with a weight average molecular weight of 250,000 and 60 parts paraffin oil (P350P by Matsumura Petroleum) were kneaded at 200°C a in a 35 mm biaxial extruder, and the kneaded mixture was cast from a coat-hanger die (1400 μm lip interval) onto a cooling roll adjusted to 30°C to produce a 1400 μm thick starting sheet. The sheet was stretched to a factor of 7 × 7 using a simultaneous biaxial stretching machine, and the paraffin oil was then extracted with methylene chloride. The extracted membrane was irradiated with a 3 Mrad ion beam in a nitrogen atmosphere with an oxygen concentration of 50 ppm. The accelerated voltage was 150 kV. The properties of the resulting microporous polyethylene membrane are given in Table 2.

Comparative Example 3

A microporous polyethylene membrane was obtained in the same manner as in Example 2 except that no organic peroxide was added. The properties of the resulting microporous polyethylene membrane are given in Table 2.

[0035]

[Table 2]

	Example 3	Example 4	Comp. Ex. 3
membrane thickness (μm)	23	29	29
porosity (%)	37	48	40
pore diameter (μm)	0.02	0.04	0.04
puncture strength (g/25 μ)	600	550	620
air permeability (sec/25 μ)	750	450	470
gel fraction (%)	0	0	0
strain-hardening	yes	yes	no
break test (160°C)	O	O	×
overcharge test 2A	O	O	break
3A	O	O	break

[0036]

[Merit of the Invention]

Because the microporous polyethylene membrane of the invention has high heat resistance, its use as a battery cell separator in particular results in better safety in terms of the fuse effect, with no restoration of current due to membrane breakage. This allows safer batteries to be provided.

[Brief Description of the Figures]

Figure 1 illustrates the relationship between time (sec) and elongation viscosity (poise) in the microporous polyethylene membranes having strain-hardening properties in Examples 1 and 2. Figure 2 illustrates the relationship between time and elongation viscosity in the microporous polyethylene membrane lacking strain-hardening properties in Comparative Example 1.

Figure 1

Figure 2

log Time (sec)

log Time (sec)

[Amendments to the original Japanese text have been incorporated in the translation.]

SYNTHETIC POLYMERIC MEMBRANES

A Structural Perspective

Second Edition

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8.2   STRETCHED SEMICRYSTALLINE FILMS

In many respects the Celgard® process, in which semicrystalline films or fibers are extruded from the melt and porosity induced by simply stretching the finished articles in the solid state, represents the ideal insofar as the manufacturing of microporous membranes is concerned. No solvents are required. Polypropylene (PP), the polymer chosen for extensive commercialization, is among the lowest-cost membrane substances and is available in a large number of specialty grades. Furthermore, production rates are believed to be high. Although the process is limited to certain slitlike pore sizes—generally ~0.2 μm in length and 0.02 μm in width—and porosities ~40% and thus lacks the extremely broad range of pore sizes and void volumes encompassed by phase-inversion membranes, nevertheless, for many applications such structures are extremely useful.

The Celgard® process is comprised of a number of interrelated steps:

1. Extrusion of film or fiber under conditions of relatively low melt temperature and high melt stress. In other words, the takeup speed is considerably greater than the extrusion rate. Under these conditions the PP molecules align themselves in the machine direction in the form of microfibrils which are believed to nucleate the formation of folded-chain row lamellar microcrystallites perpendicular to the machine direction.[6,7]

2. The row lamellae are consolidated by annealing at a temperature just below the T_m. Segmental motion is permitted which results in crystallite growth and densification as well as folding of the polymer chains at crystallite surfaces but prohibits melting which would tend to relax the lamellae and allow them to assume the more random spherulite formation which obtains under unstressed conditions. The lamellae are separated from one another by amorphous regions composed of atactic blocks or otherwise noncrystalline material in the 50% crystalline polymer. At this juncture the precursor films or fibers remain dense but exhibit different stress–strain properties (Fig. 8.1) and greater elasticity (Fig. 8.2) than comparable objects prepared from unstressed and unannealed PP. The morphology of the row lamellar precursor films or fibers are shown schematically in Figure 8.3.[8-10] In what amounts to controlled crazing, the dense precursor objects are stretched (50–300%) at a temperature above the initial annealing temperature but below the T_m. This deforms the amorphous regions between the lamellae into fibrils and results in a porous interconnecting network of slitlike voids in the machine direction (Fig. 8.3b). The dimension of the pores are defined by the drawn fibrils. They are 0.4 μm in length and 0.04 μm in width for Celgard® 2500. Porosity is 40% and pore density 9×10^9 pores/cm. However, the stretching temperature may not be critical. Indeed one patent calls for stretching at room temperature.[11] The objects become noticeably more opaque at this point and the apparent density decreases (Fig. 8.4). The extent of stretching controls both pore size and pore size distribution (Fig. 8.5). Films which are stretched only 100% have a bimodal distribution of pore sizes with many pores greater than 0.15 μm. These are more permeable than the films which are stretched 300% because the latter contain primarily pores below 0.1 μm. Stretching
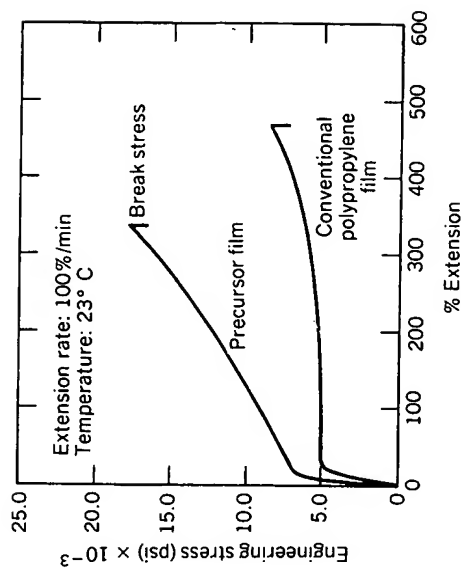
FIGURE 8.1. Stress–strain properties of precursor film prepared from isotactic polypropylene (from Bierenbaum et al.[8], reprinted with permission from *Industrial Engineering Chemistry, Product Research Development*, © 1974 American Chemical Society).

FIGURE 8.2. Recovery of precursor film from high elastic deformation (from Bierenbaum et al.[8], reprinted with permission from *Industrial Engineering Chemistry, Product Research Development* © 1974 American Chemical Society).
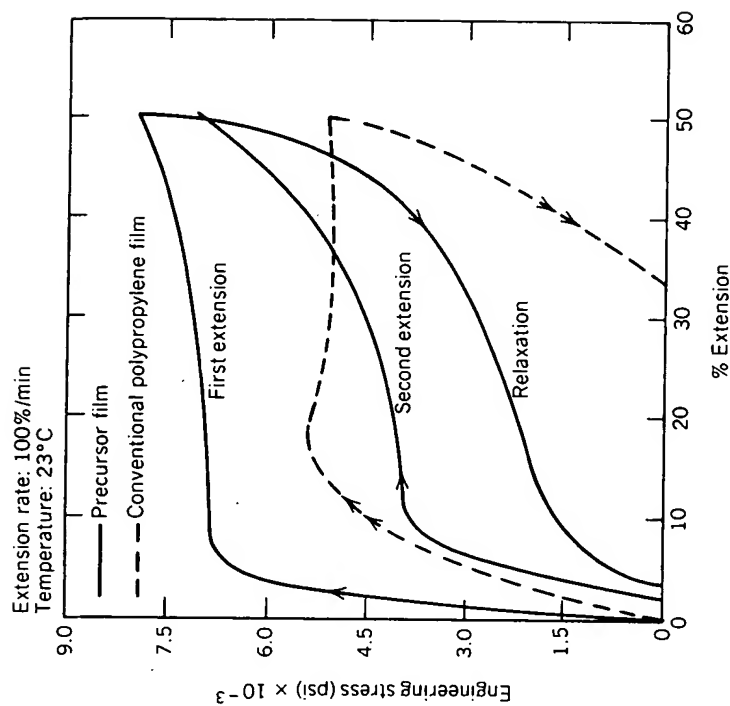
FIGURE 8.4. Apparent density of microporous polypropylene film as a function of extension (from Bierenbaum et al[8]., reprinted with permission from *Industrual Engineering Chemistry, Product Research Development* © 1974 American Chemical Society).

machine direction and the film surface. The longest dimension of the pore depends on the distance between the lamellar microcrystallites.

Although Celgard® is thin (0.025 cm thick) it can be laminated to itself to increase its stiffness and ease of handling. Its physical properties, reflecting the folding endurance characteristics of unmodified PP, are outstanding (Table 8.5). Its compatibility with various chemicals is what would be expected of unmodified PP films with a high surface area (Table 8.6).

FIGURE 8.5. Pore-size distribution in microporous polypropylene films (from Bierenbaum et al[8]., reprinted with permission from *Industrial Engineering Chemistry, Product Research Development* © 1974 American Chemical Society).
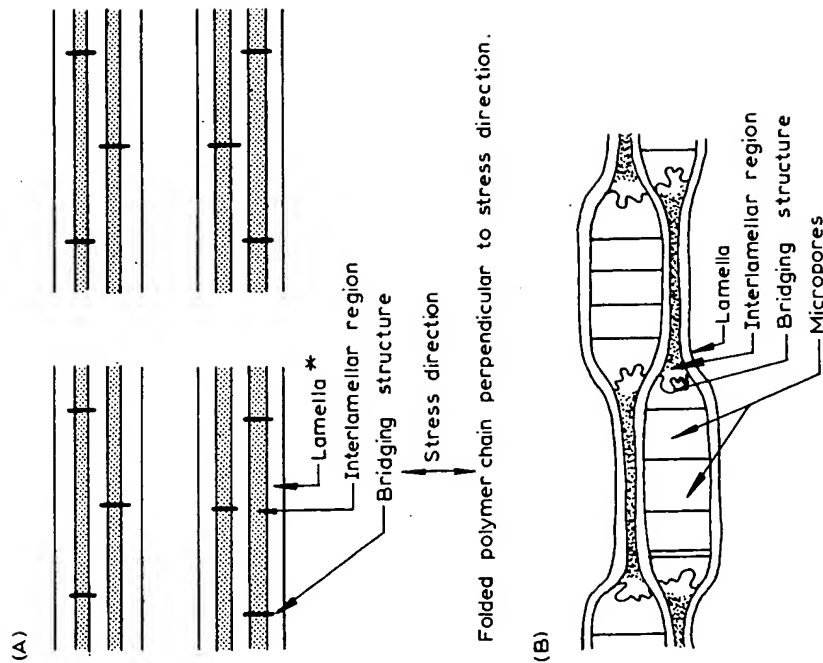

FIGURE 8.3. Schematic representation of semicrystalline morphology of (A) Celgard® precursor (extruded and annealed film), and (B) microporous Celgard® film after stretching) (from Bierenbaum et al[8]., reprinted with permission from *Industrial Engineering Chemistry, Product Research Development* © 1974 American Chemical Society).

in excess of 300% results in a precipitous loss of porosity. Finally, because the newly stretched porous films are still elastic, they are set at a temperature just below the T_m while still under tension. This minimizes subsequent loss of porosity due to creep.

The surface structure of Celgard® 2500 shows rows of elongated pores separated by unstretched lamellae (Fig. 8.6). The stretched lamellar pores are aligned horizontally, that is, in the original machine direction. Fibrillar bridging structures separate the pores from each other and the rows of pores alternate with the unstretched lamellar crystallites. The cross-sectional view of the bulk structure indicates the presence of a 0.5-μm thick surface region whose density is greater than that of the substructure (Fig. 8.7).

The three-dimensional composite view of Celgard® 2500 (Fig. 8.8) clearly shows the pores defined by drawn fibrils to be slits with the major axes parallel to the
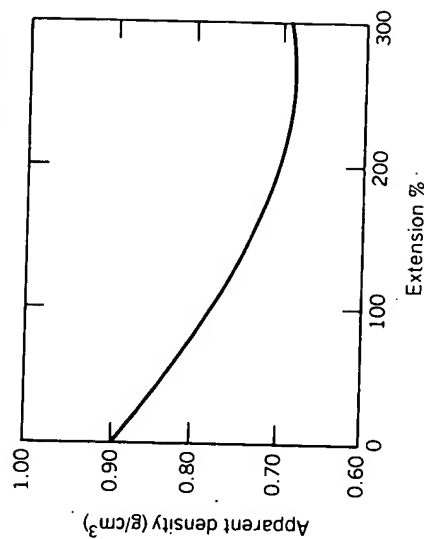
FIGURE 8.6.   High-resolution secondary electron images of Celgard® 2500 surface (from Sarada et al. [10]).

▷**FIGURE 8.7.**   TEM micrograph of surfactant/OsO₄ treated cross section of Celgard® 2500 (from Sur-ada et al. [10]).

Celgard® is available in both film and hollow-fiber form. Celgard® 2400 and Celgard® 2500 are hydrophobic films with effective pore size (pore-width dimensions) of 0.02 and 0.04 μm, respectively. Two-ply forms are also available as are various composite laminates to nonwoven polyproplyene fabrics. The corresponding hydrophilic (surfactant-containing) grades are Celgard® 3400 and Celgard® 3500.

The two hydrophobic microporous hollow-fiber grades, Celgard X-10 and X-20, differ in porosity, ~20 and 40%, respectively, but not in effective pore size (0.03 μm). They both have MW cutoffs of approximately 100,000 daltons. Celgard X-10 is available in 100, 200, and 240-μm ID 25-μm wall thickness. One particular area, where these fibers are expected to dominate is in hollow-fiber blood oxygenators.

Gore-Tex® microporous poly(tetrafluoroethylene) (PTFE), [12,13] is one of the most

TABLE 8.6   COMPATIBILITY OF CELGARD FILM WITH VARIOUS COMPOUNDS[a,b]

Acids			Halogenated Hydrocarbons	
H₂SO₄ (concd)	A		Carbon tetrachloride	C
Alcohols			Tetrachloroethylene	C
Ethyl alcohol	A		(perchloroethylene)	
Ethylene glycol	A		Hydrocarbons	
Isopropyl alcohol	A		Benzene	B
Ether alcohols			Hexane	B
Butyl Cellosolve	B		Toluene	B
(2-butoxyethanol)			Ketones	
Methyl Cellosolve	A		Acetone	A
(2-methoxyethanol)			Methyl ethyl ketone	A
Bases			Oils	
KOH (40%)	A		10W30 motor oil	B
Ethers			Miscellaneous	
1,4-dioxane	B		NN-dimethylacetamide	A
Fuels			N,N-dimethylformamide	B
Gasoline	B		Nitrobenzene	B
Kerosene	B		Tetrahydrofuran	B
			Freon TF	B

[a]From Bierenbaum et al.[8] Reprinted with permission from *Industrial Engineering Chemistry Product Research Development*, © 1983 American Chemical Society.

[b]The compatibility statements are based on 72 h of exposure at room temperature (25°). Key: A, good (no effect); B, slight swell; C, material swells, separation characteristics should be evaluated.

important of the porous membranes manufactured by a process other than phase inversion. Gore-Tex® also resembles Celgard® in that they both contain characteristic slitlike pores (Figs. 8.9 and 8.10). This is because both processes utilize stretching to introduce porosity. The fact that the slits in Gore-Tex® are not always parallel to one another is attributable to the fact that biaxial stretching is sometimes employed. Since PTFE cannot be melt extruded, a highly (~98.5%) crystalline dispersion polymer of 500,000 MW and fine (0.1 μm) fiberlike structures, Teflon® 6A, is mixed together with 15–25% of a lubricant such as naphtha or kerosene and

then ram extruded. The lubricant is then removed by heating, after which the sheet is reduced in thickness by passing between calender rolls at 80°C. Uniaxial or biaxial stretching is followed by sintering at 327°C. During the sintering process the amorphous content increases and serves to "lock in" and strengthen the pores in the stretched membrane. The Gore-Tex® process is versatile and capable of producing membranes with pore-size and porosity ranges which rival those of phase-inversion membranes (Table 8.7). Gore-Tex® membranes are also available in laminated composites with a variety of support substrates. They represent the most chemically inert and hydrophobic synthetic polymeric membranes and are unique in their ability to filter organic solutions and hot inorganic acids and bases which are vital to the electronics industry.

8.3   SINTERED-PARTICLE MEMBRANES

Sintering refers to any change in shape undergone by a small particle or a cluster of particles of uniform composition when held at an elevated temperature.[14] In producing membranes by the sintering process, finely divided particles (spherical or fibrous in shape) are heated to a temperature at or below the melting range of the material. As the exterior surface of the particles soften or melts, capillary pres-

FIGURE 8.7.   (Continued)

TABLE 8.5   TYPICAL PHYSICAL PROPERTIES OF CELGARD FILM[a]

Property	Value	Test Method
Tensile strength, MD[b]	20,000 psi	ASTM D882
TD[c]	2,000 psi	
Tensile modulus, MD	2 × 10⁵ psi	ASTM D882
Elongation, MD	40%	ASTM D882
Tear initiation, MD	1 lb	ASTM D1004
MIT fold endurance	10⁵	ASTM D643
Mullen burst	20 points	ASTM D774

[a]From Bierenbaum et al.[8] Reprinted with permission from *Industrial Engineering Chemistry Product Research Development*, © 1983 American Chemical Society.

[b]MD = machine direction.

[c]TD = transverse to machine direction.

TABLE 7.3 EFFECT OF RELATIVE HUMIDITY UPON PERMEABILITY AND PORE SIZE[a]

Relative Humidity at 20°C (%)	Filtration Time[b] (sec)	Average Pore Diameter (nm)
80	25–40	~600
60	40–60	~500
40	60–80	~400

[a]From Maier and Scheuermann[4]
[b]For 500 mL H_2O/12.5 cm² at 70 cm Hg

TABLE 7.4 INFLUENCE OF CASTING SOLUTION WATER CONCENTRATIONS UPON PORE SIZE AND PERMEABILITY OF COLLODION MEMBRANES[a]

H_2O Concentration in Casting Solution (%)	Filtration Time[b] (S)	Average Pore Diameter (nm)	Casting-Solution Viscosity at 20°C (cps)
3.3	40	600	2011
0.4	800	30	1813
0.0 (trace)	4000	15	1600

[a]From Maier and Scheuermann[4]
[b]For 500 mL H_2O/12.5 cm² at 70 cm Hg.

porosity during drying and less likely to be wet → dry reversible. Since the dry process tends to employ more dilute solutions and less compatible pore formers (both of which characteristics promote the formation of microgels) than does the wet process, the former is more likely to produce microgels than the latter. However, there are many exceptions to this rule and it is possible both to produce microgels by a wet process and ultragels by a dry process.

7.3 THE WET PROCESS

The wet or combined evaporation–diffusion technique is that variation of the phase-inversion process in which a *viscous* polymer solution is either (1) allowed to partially evaporate after which it is immersed into a nonsolvent gelation bath where whatever is left of the solvent–pore-former system is exchanged for the nonsolvent or (2) is immersed directly into the nonsolvent gelation bath for the exchange of the solvent system for nonsolvent. The end products of the wet process are water-swollen membranes; moreover, the water content of membranes—the equivalent of porosity in the dry process—is a prime determinant of its functional performance characteristics. *It is therefore fundamental to consider the effects of such variables*

RE 7.12. SEM photomicrograph of a cross section of a dry cellulose acetate membrane with an egral substructure (from Kesting et al.[14]; © 1965).

E 7.2 EQUIVALENT NONSOLVENT CONCENTRATIONS IN ACETONE AND OLANE SOLUTIONS[a] FOR DRY-RO BLEND MEMBRANES OF CA AND THE TMA OF CA 11-BROMOUNDECANOATE

nt	Boiling Point (°C)	Δbp (°C)	Nonsolvent Concentration (g IBA/formulation)	Permeability[a] (gal/ft² day)	Salt[b] Rejection (%)
ne	56	54	38	5.6	97.9
olane	75	35	54	5.5	97.8

polymer concentration, 10% wt/vol; polymer ratio, 6/1 JLF-68CA/TMA salt of CA 11-bromodecanoate (made from E-383-40 CA with 0.3-DS (quaternary ammonium groups); methanol, 10 nulation.

NaCl feed at 400 psi and 25 ± 1°C.

as casting-solution composition and environmental parameters in terms of their effects upon membrane-water contents.[14,15]

A wet-process solution must be relatively viscous ($\geq 10^4$ cps) at the moment of immersion in the nonsolvent so that it will retain its integrity throughout gelation. When it is too fluid, the primary gel will be subject to disruption by the weight of the nonsolvent and the uneven forces brought about by the various currents which come into play during immersion. The requirement for high viscosity and hence high polymer concentration is in most cases inconsistent with the attainment of high porosity via the inclusion of nonsolvent pore formers. Therefore, when they are required, pore formers which are utilized in wet-process casting solutions are frequently chosen from the swelling agent—weak solvent side of the polymer–solvent interaction spectrum (Chapter 5). Moreover, the presence of pore formers within the casting solution prior to its immersion into a nonsolvent gelation bath is not a requirement of every wet-process solution. In many instances, particularly when nonvolatile solvents with a strong affinity for the nonsolvent in the gelation bath are utilized, the phase-inversion sequence Sol 1 → Sol 2 → gel is evoked by the simple act of immersion into nonsolvent. In such a case the nonsolvent bath represents an *external* source of incompatibility and a two-component solution (polymer + solvent) becomes in effect a three-component solution (polymer + solvent + nonsolvent pore former) as a result of the diffusion of the nonsolvent into, and the solvent out of, the nascent membrane gel.

The effect of the strong nonsolvent, water, may be influenced by other components of the casting solution. The presence of lyotropic salt swelling agents from the Hofmeister series causes the aggregation of water molecules about the electrophilic cations, thereby considerably modifying the properties of the water so affected.[14] The result of this interaction is to change the role of water from that of a nonsolvent to that of a swelling agent (Table 7.5). Other polar nonsolvents such as the aliphatic alcohols function in much the same manner as water, except that their nonsolvent tendencies are less pronounced. The role of water in the atmosphere and in the solution to effect gross structural irregularities will be discussed later in this chapter.

The effects of increasing the concentration of the weak nonsolvent pore former, ethanol, in a casting solution containing CA and acetone is to increase the porosity of the resultant membranes (Table 7.6, Fig. 7.13). (Because of their excellent solubility, certain cellulosic polymers can be so formulated that their solutions represent exceptions to the rule that wet-process solutions require highly compatible pore formers). As the concentration of ethanol is increased, the values of δ_p decrease slightly and the values of δ_h increase appreciably, which has the effect of bringing the solution closer to the point of incipient gelation, that is, to the perimeter of the solubility envelope. Since a solution which contains a high concentration of nonsolvent can be presumed to be of the Sol 2 type close to gelation, its immersion into a nonsolvent bath and subsequent gelation will be accompanied by less gel contraction than would occur if the solution were further removed from the perimeter of the solubility map. The result is that porosity and permeability increase as the concentration of pore former increases. Because the pore former is

TABLE 7.5 CASTING SOLUTION WATER-CONCENTRATION EFFECTS[a]

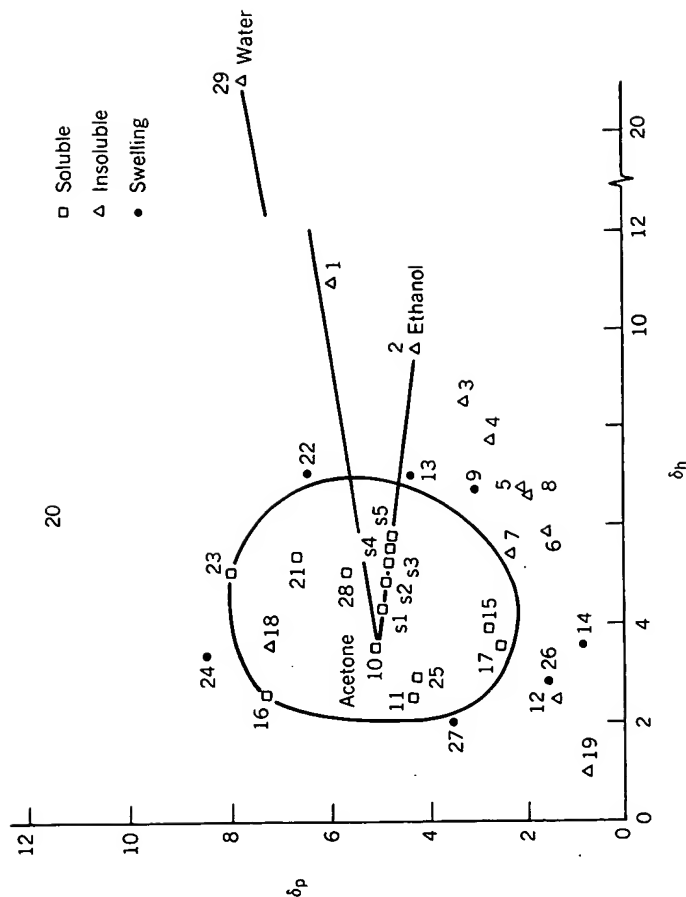| Water Concentration (g/formulation)[b]	Swelling-Agent Concentration (g ZnCl₂/formulation)[b]	Description of Membrane	Wet Thickness of Unheated Membrane (mm × 10²)	Gravimetric Swelling Ratio of Unheated Membrane (wet wt/dry wt)	Rate of Water Transport (mL/cm² day)[c]		Salt Retention (%)
					Deionized-Water Feed	0.6 M NaCl Feed	
0	0	Brittle, opaque (microgel)	5.8	1.47	<1	—	—
5	0	Brittle, opaque (microgel)	6.4	1.77	<1	—	—
10	0	Brittle, opaque (microgel)	7.1	1.99	<1	—	—
15	0	Brittle, opaque (microgel)	8.0	2.35	<1	—	—
0	5	Clear (microgel)	8.7	2.53	24	16	90.3
5	5	Opalescent (ultragel)	9.0	2.79	34	22.8	97.2
10	5	Opalescent (ultragel)	9.2	2.85	72	48	98.5
15	5	Opalescent, opaque (ultra gel–microgel)	9.6	2.92	136	82	96.2

[a] From Kesting et al.,[15] © 1965.

[b] Formulation: cellulose acetate, 22.2 g; acetone, 66.7 g (doctor-blade gap, 0.25 mm).

[c] Rate of water transport and salt retention at 102-atm pressure for heated membranes (86°C for 5 min).

of a nonsolvent type, solution compatibility decreases with increasing ethanol concentration. This leads ultimately to increased diameters in the micelles of So... and consequently to greater opacity in the final membrane. It is worthy of note t... it is only the insufficient Δbp of 23°C between acetone and ethanol which preve... this solution from being a candidate for the dry process. If methyl formate (... 30°C) or propylene oxide (bp 35°C) had been employed as solvents in conjuncti... with ethanol as the pore former, this solution could have served in either a wet-... a dry-process mode. If acetone had been utilized as a solvent in conjunction w... propanol (bp 97°C) or isobutanol (bp 108°C) as pore formers, the same would... course apply.

The effects of increasing the concentration of the solvent-type pore form... formamide, upon the porosity, optical, and permeability properties of CA mer... branes are found in Table 7.7. In the first place, the utilization of this solution... the dry-process mode leads to the formation of a dense film. Since both aceton... and formamide are solvents, the loss of the more volatile acetone leaves behind... high-boiling solvent, formamide, which plasticizes the CA gel as it evaporates. T... fact that [η] increases and both solution and membrane turbidity decrease wi... increasing concentration of formamide in the acetone–formamide solvent syste... suggests that solvent power increases as well. Concurrent increases in thickness... porosity, and permeability are attributable to the strong hydrogen-bonding capaci... of formamide coupled with its strong affinity for solvating CA. After immersion... desolvation of such solutions is slow rather than rapid because water can associat... with formamide by hydrogen bonding, thereby lessening water's role as a stron... nonsolvent. The net result appears to be that the Sol 2 → gel transition occurs ... a reduced rate during which the aggregating mass is more amenable to the infusio... of a higher concentration of nonsolvent than would otherwise be possible in th... case of a more abrupt Sol 2 → gel transition.

The gelation bath temperature also exerts an important influence upon the struc...

TABLE 7.7 PROPERTIES OF SOLS AND GELS FROM ACETONE–FORMAMIDE SOLUTIONS OF CA[a]

Formamide Concentration (mol %)	Sol[b] Properties			Gel Properties			
	[η]25°C	Turbidity at 546 μm (x 10²)	Turbidity at 546 μm (x 10⁻¹)	Thickness (μm)	Wet wt / Dry Wt	Water] (cm/d
0	0.895	1.6	38.7	36	1.71	No fl
10	0.942	0.9	33.2	43	2.10	No fl
20	0.948	0.6	—	46	3.01	2
30	0.963	0.5	20.7	74	3.44	12
40	—	0.45	7.8	86	3.90	38
50	—	0.45	1.4	94	4.40	132

[a]Adapted from Kesting and Menefee.[17]
[b]15 g E-398-10 CA/100 mL solution.
[c]Distilled-water feed at 40.8 atm and 25°C.

TABLE 7.6 EFFECT OF SWELLING AGENT (ETHANOL) ON THE MEMBRANE-WATER CONTENT[a]

Membrane Code No.	Mixed Solvent		Calculated δ Values of Mixed Solvents		Membrane-Water Content (wt %)
	Ethanol (mol %)	Acetone (mol %)	δ_p	δ_h	
CA-24	20	80	4.99	4.23	50.7
CA-23	30	70	4.93	4.69	50.3
CA-22	40	60	4.86	5.20	53.4
CA-25	46.6	53.4	4.83	5.47	61.2
CA-21	50	50	4.79	5.75	65.8

[a]From Chawla and Chang[16]; © 1975.

FIGURE 7.13. Solubility diagram for cellulose acetate. Solvents used: (1) methanol, (2) ethanol, (3) propanol, (4) butanol, (5) 1-pentanol, (6) 1-octanol, (7) 2-octanol, (8) cyclohexanol, (9) benzyl alcohol, (10) acetone, (11) methyl ethyl ketone, (12) diethyl ether, (13) ethylene glycol monoethyl ether, (14) dioxane, (15) tetrahydrofuran, (16) furfural, (17) ethyl acetate, (18) ethyl sulfate, (19) toluene, (20) formamide, (21) N,N-dimethyl formamide, (22) diethylene triamine, (23) dimethyl sulfoxide, (24) acrylonitrile, (25) pyridine, (26) chloroform, (27) 1,2-dichloroethane, (28) acetic anhydride, and (29) water (from Chawla and Chang[16]).

ture and function of HF membranes (Table 7.8). Increasing temperature hastens the onset of gelation which in turn results in increased void size, degree of swelling, and permeability, and decreased permselectivity.

Increasing the evaporation (drying) time prior to immersion in the nonsolvent medium causes a decrease in cell size and porosity and hence a decrease in permeability (Table 7.9). Permselectivity first increases and then decreases owing to stress imposed on the skin layer and possibly also to some swelling and rehardening of the skin as the solvent concentration in the nonsolvent bath increases.

The higher the affinity of the gelation medium for the components of the casting solution, the more gradual will be the Sol 2 → gel transition and the greater will be porosity in the final membrane. Thus the gelation of a CA solution in methanol will lead to a membrane of higher porosity than the gelation of the same solution in water. Methanol has greater affinity for CA than does water. Conversely, water is a stronger nonsolvent for CA than is methanol. Because the immersion of a casting solution in a strong nonsolvent such as water often leads to a skinned membrane it may be expedient, when a skinless membrane is desired, to immerse the casting solution into a nonsolvent solution which contains some solvent. Likewise, when a skinned membrane is available by any process, the skin may often be removed by immersing it into a nonsolvent/solvent solution. A closely related phenomenon known as *clearing* is utilized to collapse an opaque microporous electrophoresis membrane into a clear dense film so that the electrophoretogram can be read on an optical densitometer without changing the spacial relationships between the various protein fractions. Here the reverse of the dry casting process is employed. Instead of utilizing a volatile solvent and a nonvolatile nonsolvent to gradually decrease compatibility, a volatile nonsolvent and a nonvolatile solvent are employed to gradually increase the affinity of the clearing solution for the membrane substance as drying progresses. Gravity does the rest as the softened but intact gel slowly collapses.

The structure which is at hand immediately following the Sol 2 → gel transition in the dry process is known as a primary gel. It is seldom isolated as such because with continued evaporation (± syneresis) and drying the completely consolidated membrane, known as the secondary gel, is ordinarily the only product which is encountered or of interest. This is not usually the case for the wet process, however. Here, after the viscous solution has been gelled by immersion and the solvent system has been removed from the gel, a primary gel membrane which is stable as such for an indefinite period is the result. Such a membrane is easily distinguished from the secondary gels which result after the primary structures have been subjected to various postformation treatments.

As was the case for the dry process, the control of primary gel structure by environmental and especially casting-solution variables permits far greater latitude in the regulation of ultimate structural and performance characteristics of wet phase-inversion membranes than does the modification of primary into secondary gels. Because the properties of the primary gel determine to a large extent those of its secondary counterpart, the former should be considered as the more fundamentally characteristic and important structure in any consideration of the effects of varia-

TABLE 7.8 GELATION-BATH TEMPERATURE EFFECTS[a,b]

Gelation-Bath Temperature (°C)	Membrane Appearance	Intrinsic Viscosity [η] of Cellulose Acetate in Acetone–Water (66.7:100)[c]	Wet Thickness of Unheated Membrane [(mm) × 10²]	Gravimetric Swelling Ratio of Unheated Membrane (wet wt/dry wt)	Rate of Water Transport mL/cm² day)[d]		Salt Retention (%)
					Deionized-Water Feed	0.6 M NaCl Feed	
0	Opalescent	0.985	9.2	2.85	84	50	98.6
10	Opaque	0.940	14.0	3.80	83	50	97.1
25	Opaque	0.05	22.8	5.80	90	58	90.1
40	Opaque	0.745	31.0	6.98	118	74	81.1

[a]From Kesting et al.[15]; © 1965.

[b]Casting-solution composition: cellulose acetate, 22.2g; acetone, 66.7 g; water 10.0 g; ZnCl₂, 5.0 g (doctor-blade gap, 0.25 mm).

[c]Measured at the corresponding gelation-bath temperature.

[d]Rate of water transport and salt retention for heated membranes (86°C for 5 min).

tions in fabrication parameters, for example, casting-solution composition, upon performance characteristics. Once a primary gel has been formed, it may be utilized as such (particularly for low-pressure applications), or it may be subjected to various physical and/or chemical treatments for conversion into a secondary gel which may be more suitable for a given end use.

Physical modifications of primary gel structures can be effected either to increase or to decrease the porosity (degree of swelling, void volume, water content, etc.), pore size, permeability, and permselectivity. The technique utilized to produce porous membranes from dense films can be used to effect an increase in porosity. In this variation of Brown's[18] technique (Chapter 8), an already porous primary gel is immersed in a swelling medium. To set the secondary gel in its more expanded condition the swelling medium is removed, either by exchange with a nonsolvent (nonsolvent–swelling-agent miscibility is essential) or by simple evaporation.

Since this technique adds another step to the fabrication process and is complicated by the leaching of low-molecular-weight polymer from the primary gel by the swelling medium, it is usually circumvented by the reformulation of the casting solution to produce a primary gel with an initially higher void volume. It is frequently encountered, however, as an undesirable factor in the permeation of certain organic solutes which interact with and swell the membrane, thereby altering initial pore characteristics and permeability. Of much greater practical importance are physical alterations of the primary gel structure to effect decreases in porosity. The most important means to this end are thermal annealing, pressurization, and solvent shrinking.

Annealing a porous membrane (particularly one which contains a nonsolvent capable of functioning to some extent as a plasticizer) results in a diminution of void volume and permeability and, because pore size is generally decreased as well, an increase in permselectivity. The reason for this can be seen on the molecular level where the introduction of thermal energy causes translational motion of the macromolecules, with the result that polar groups on the same and/or on neighboring molecules will approach one another closely enough to form virtual cross-links by dipole–dipole interactions. These cross-links tend to decrease chain mobility and, in a nonsolvent medium, are irreversible because of the inability of the nonsolvent to solvate and therefore intervene between the polar groups so enjoined.

Annealing has some effects which are continuous and some which are discontinuous. A continuous effect is the loss in water content and void volume with increasing temperature (Fig. 7.14). Water is lost from the primary gel during annealing, both because of the formation of virtual cross-links and because of the decrease in hydrogen bonding and cluster size in the water itself. An example of a discontinuous effect is the dramatic increase in permselectivity (salt retention) which is observed when cellulose acetate membranes are heated above 68.6°C, the glass transition temperature (Fig. 7.15). In fact, not one but two discontinuities are found on the permselectivity versus annealing temperature curve for cellulose acetate desalination membranes. The first signals an increase, and the second a decrease, in permselectivity. The increase, on the basis of the previously cited structural

TABLE 7.9 DRYING TIME EFFECTS[a,b]

Drying Time[c] (min)	Description of Membrane	Wet Thickness of Unheated Membrane (mm) × 10[2]	Gravimetric Swelling Ratio of Unheated Membrane (wet dry/dry wt)	Deionized-Water Feed	0.6 M NaCl Feed	Salt Retention (%)
				Rate of Water Transport (mL/cm²·day)[d]		
1	Opaque–opalescent (microgel blending into ultragel)	13.9	2.88	116.	72	98.0
3	Opalescent (ultragel)	12.2	2.98	84	50	98.6
5	Opalescent (ultragel)	10.2	2.65	86	54	98.8
10	Opalescent–clear (ultragel)	8.5	2.41	80	50	96.3
20	Clear (ultragel)	5.8	1.75	72	50	75.1
30	Clear (ultragel)	5.3	1.60	50	36	71.5

[a] Kesting et al.[15], © 1965.
[b] Casting-solution composition: cellulose acetate, 22.2 g; acetone, 66.7 g; water, 10.0 g; ZnCl₂, 5.0 g (doctor-blade gap, 0.25 mm).
[c] Drying time—interval between casting at −11°C and immersion into gelation bath (0°C).
[d] Rate of water transport and salt retention at 102 atm pressure for heated membranes (86°C for 5 min).
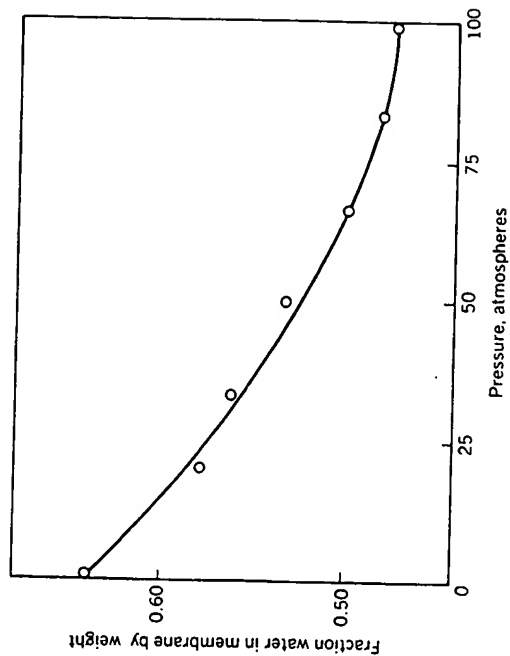
FIGURE 7.16.   Membrane-water content as a function of pressure (from Kesting et al.[15]).

interpretation, may be attributed to the attainment of the critical interchain spacing or pore diameter, whereas the decrease may be related to disruption in the uniformity of these spacings owing to closer alignment of polymer chains in the glassy state in some regions at the expense of strain-induced removal of polymer chains from one another in others.

Whereas heating causes shrinkage in three dimensions, the application of pressure causes shrinkage primarily in one dimension, namely in the plane perpendicular to the surface. Two stages may be distinguished in the shrinkage of porous membranes under pressure (Fig. 7.16): (1) The rapid loss of void volume by the porous substructure which occurs at comparatively low pressures; and (2) the slower, more gradual loss of void volume by the comparatively dense skin layer. Inasmuch as the skin layer more closely approaches the structures of the bulk polymer, it is to be expected that significant compaction of this layer will require pressures in excess of the compressive yield point.

7.4   THE THERMAL PROCESS

A significant recent development in the technology of phase-inversion membranes is the invention of the thermal process by Castro.[19] The thermal process is applicable to a wide range of polymers, which because of their poor solubility, are otherwise inaccessible to the phase-inversion approach. In essence, the thermal process utilizes a latent solvent, that is, a substance which is a solvent at elevated (~220°C) temperatures and a nonsolvent at lower temperatures, and thermal energy to produce a Sol 1 which on cooling inverts into a Sol 2, and on further cooling, gels. The reason for the incompatibility which evokes Sol 2 is loss of solvent power
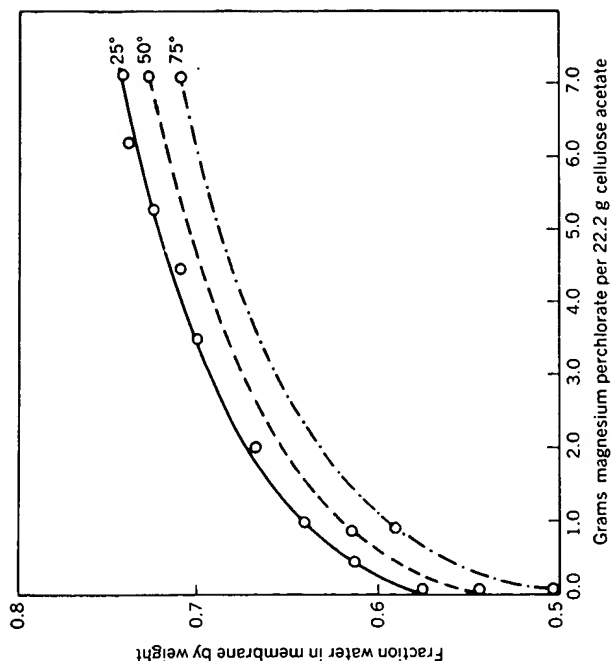

FIGURE 7.14.   Membrane-water content as a function of temperature (from Kesting et al.[15]; © 1965).
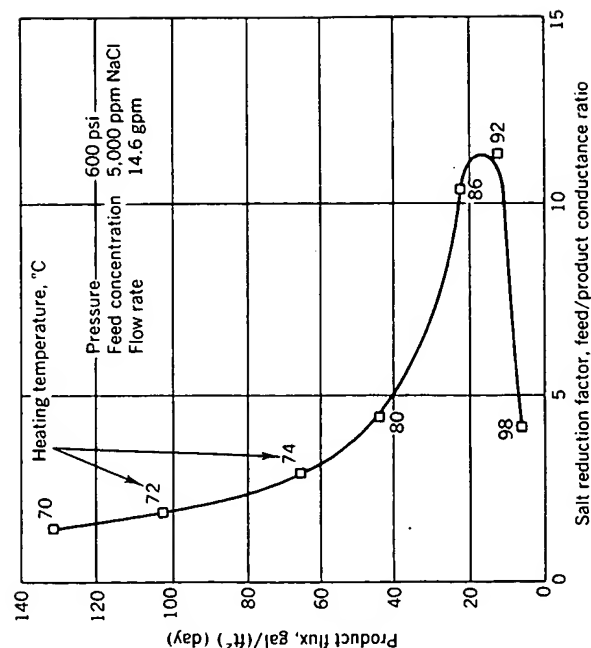

FIGURE 7.15.   Permeability versus permselectivity for Loeb–Sourirajan membranes annealed at various temperatures.